[NAME OF DOCUMENT] SPECIFICATION

[TITLE OF THE INVENTION] SEMICONDUCTOR DEVICE WITH Kr-CONTAINING SILICON OXIDE FILM INTEGRATED THEREINTO, AND MANUFACTURING METHOD OF THE SILICON OXIDE FILM

[WHAT IS CLAIMED IS:]

[CLAIM 1]

A semiconductor device including a plurality of transistors with their substrate of silicon, characterized in that

at least part of a silicon oxide film formed on a surface of said silicon contains Kr.

[CLAIM 2]

The semiconductor device characterized in that

a recessed groove is formed at part of said substrate surface between said plurality of transistors, and a dielectric substance is formed in part of said groove,

said silicon oxide film is formed on a corner of said substrate surface in said groove, and at least part of said silicon oxide film contains Kr.

[CLAIM 3]

The semiconductor device according to claim 1 or 2, characterized in that a side wall portion in said groove is formed such that the angle of part of said side wall portion with said substrate surface exceeds at least 75 degrees.

[CLAIM 4]

The semiconductor device according to claim 1 or 2, characterized in that the difference in thickness

of said silicon oxide film between the portions formed on at least part of the surface other than said groove of said substrate and on at least part of the surface in said groove is within 30%.

[CLAIM 5]

A semiconductor device wherein a semiconductor film at part of a surface of which a recessed groove is formed or an island-shape semiconductor film is formed on an insulating film, characterized in that

a silicon oxide film is formed on a corner of said semiconductor film of said groove or a corner of said semiconductor film, and at least part of said silicon oxide film contains Kr.

[CLAIM 6]

The semiconductor device according to any one of claims 1 to 5, characterized in that the content of Kr contained in said silicon oxide film decreases from said silicon oxide film surface toward a silicon/silicon oxide film interface.

[CLAIM 7]

The semiconductor device according to any one of claims 1 to 5, characterized in that the Kr content in said silicon oxide film is 5×10^{11} cm^{-2} or less at the surface density.

[CLAIM 8]

A method for forming a silicon oxide film, characterized by introducing a mixture gas mainly containing a gas containing oxygen and Kr gas into a process chamber, exciting plasma with a microwave,

and directly oxidizing a silicon substrate surface placed in the process chamber, thereby forming the silicon oxide film containing Kr recited in any one of claims 1 to 5 on said silicon substrate surface.

[CLAIM 9]

The method for forming a silicon oxide film according to claim 8, characterized in that the oxygen partial pressure in said mixture gas is 2 to 4%, and the pressure in said process chamber is 800 mTorr to 1.2 Torr.

[CLAIM 10]

The method for forming a silicon oxide film according to claim 9, characterized in that the plasma in claim 4 is plasma excited with a microwave of a frequency of 900 MHz to 10 GHz.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[FIELD OF THE INDUSTRIAL AVAILABILITY]

The present invention relates to semiconductor devices using silicon oxide films and methods for forming silicon oxide films, particularly to semiconductor devices using very thin silicon oxide films, semiconductor devices including element isolation structures in which a dielectric substance is buried in silicon, semiconductor devices including element isolation structures formed on an insulating film, and methods for forming semiconductor devices.

[0002]

[CONVENTIONAL ART]

The gate insulating films of transistors formed on silicon substrates require high performance characteristics such as low interface level density, and high reliability such as high withstand voltage and high hot carrier tolerance. As a conventional oxide film formation technique to meet those requirements, thermal oxidation at 800°C or more has been used.

[0003]

Besides, from a demand for forming transistors on a silicon semiconductor at higher density, for transistor integrated elements formed on a silicon substrate, in concert with the progress of scale-down technique, in place of selective oxidation film (LOCOS) element isolation structures in which bird's beaks extend, element isolation structures such as shallow trench isolation that enables narrow dielectric isolation came to be used.

[0004]

Besides, for integrated elements such as SOI (Silicon On Insulator) transistors and polysilicon transistors formed on an insulating film, used were element isolation structures in which silicon films are formed into islands by LOCOS isolation with silicon oxide films and mesa isolation by etching silicon off.

[0005]

[PROBLEMS WHICH THE INVENTION IS TO SETTLE]

For formation of semiconductor elements with ultrahigh integration/ultrahigh speed drive, however, conventional thermal oxidation can not be used. To realize ultrahigh speed elements, a metallic material must be introduced in the semiconductor device. But, if a high temperature process at 550°C or more is used, the metal can react with the semiconductor to deteriorate the operation performance of the elements. Besides, if such a high temperature process is used, it becomes difficult to form an accurate impurity distribution because of rediffusion of impurities. This makes it hard to form ultrahigh integrated elements. Therefore, oxide film formation at a low temperature of 550°C or less is indispensable.

[0006]

So, in recent years, techniques for forming silicon oxide films at low temperatures have been studied. But, characteristics of a silicon oxide film formed at 550°C or less were never equal to those of a thermal oxide film. The oxidation speed of such conventional low-temperature oxidation is lower than that of thermal oxidation, so electrical characteristics, such as interface level density and current-voltage characteristic, of a silicon oxide film formed were greatly inferior to those of a thermal oxide film.

[0007]

Besides, in a conventional element isolation

structure for transistor integrated elements formed on a silicon substrate, the thickness of a silicon oxide film at a portion near a corner of an element isolation side wall portion is smaller than that on a flat silicon surface portion. Therefore, a problem arose that characteristics such as leakage current and withstand voltage of the oxide film are inferior at the thin portion and the reliability in performance of the elements are deteriorated. Further, since a parasitic transistor element having its thin gate oxide film exists in parallel with a transistor element having its gate oxide film of a normal thickness, this deteriorated the voltage-current characteristic of the transistor.

[0008]

In order to solve such problems, if the thickness of the silicon oxide film is simply increased to avoid the problem that arises at the thin portion, since the silicon oxide film also serves as a gate oxide film, a problem arises that the drive performance of the MOS transistor deteriorates. So, conventionally, the angle of the side wall portion of the recessed portion in the element isolating region with the silicon surface is set at about 70 degrees or less so that thinning of the silicon oxide film at corners of the side wall portion is relieved. Even in this case, however, about 30% or more thinning occurred, and occurrence of characteristic deterioration such as leakage current and withstand

voltage of the oxide film at the thin portion could not completely be prevented. Furthermore, formation of the recessed element isolating region with an obtuse angle brought about problems that the element isolation width increased, the ratio in area of the effective region where elements such as transistors are to be formed decreased, and high density integration could not be intended.

[0009]

Furthermore, in a conventional element isolation structure for integrated elements such as SOI (Silicon On Insulator) transistors and polysilicon transistors formed on an insulating film, in case of LOCOS element isolation, a parasitic transistor element existed near the interface between the element isolation oxide film below a gate electrode and silicon. This deteriorated electrical characteristics of the transistor, in particular, subthreshold current characteristic and off-leak characteristic. On the other hand, in case of mesa element isolation, a high quality oxide film could not be formed on the element isolation side wall portion where silicon has been etched off. This had a bad influence on characteristics, in particular, off characteristics, of the transistor.

[0010]

[MEANS FOR SOLVING THE PROBLEMS]

The present invention was made for solving those conventional problems. It is an object of the present

invention to form a uniform silicon oxide firm of a high quality on the surface of a substrate at a low substrate-temperature of 200-500°C and to provide semiconductor device using a silicon oxide film, and a semiconductor device of the present invention includes a plurality of transistors with their substrate of silicon, and is characterized in that at least part of a silicon oxide film formed on a surface of said silicon contains Kr.

[0011]

[OPERATION]

According to the present invention, it is possible to realize silicon oxide films having, even though they were formed by low-temperature plasma oxidation, characteristics and reliability superior to those of silicon thermal oxide films formed at a high temperature of about 1000°C, and to realize high-performance transistor integrated circuits.

[0012]

According to the present invention, since the thickness of the silicon oxide film at a portion near a corner of a silicon oxide film element isolation side wall portion becomes generally equal to the thickness of a flat silicon surface portion, the characteristics such as leakage current and withstand voltage of the oxide film become good, and an improvement of the reliability of the element and an improvement of the drive performance of the MOS transistor can be realized. Besides, even if the

angle of the side wall portion of the recess portion of the element isolating region formed on a silicon substrate, with the silicon surface is set at 70 degrees or more or 90 degrees, thinning of the silicon oxide film at a corner of the side wall portion does not occur, it becomes possible to form a narrow element isolating region, the ratio of an effective area for forming elements such as transistors is increased, and high density integration can be realized.

[0013]

Further, even in the element isolation structure for integrated elements of SOI (Silicon On Insulator) transistors and polysilicon transistors formed on an insulating film, a high-quality oxide film can be formed on the element isolation side wall portion, and, without any parasitic transistor existing, the electrical characteristics of the transistors can be good.

[0014]

An embodiment of the present invention will be described below.

[EMBODIMENT 1]

[0015]

Low-temperature oxide film formation using plasma will be described first. Fig. 1 is a sectional view showing an example of apparatus using a radial line slot antenna for realizing an oxidation method of the present invention (refer to Japanese Patent

Application No. 9-133422). The present invention has a novel characteristic feature wherein Kr is used in plasma-exciting gas. This apparatus is mainly effective for a circular substrate. A vacuum vessel (process chamber) 101 is made vacuous, Kr gas and O_2 gas are introduced through a shower plate 102, and, for example, the pressure in the process chamber is set at about 1 Torr (133 Pa). A circular substrate 103 such as a silicon wafer is placed on a sample table 104 with a heating system, and, for example, setting is made such that the temperature of the sample becomes 400°C. If this temperature setting is within the range of 200 to 500°C, the same result as that described below can be obtained. A microwave of 2.45 GHz is supplied from a coaxial waveguide tube 105 through a radial line slot antenna 106 and a dielectric plate 107 into the process chamber, and high density plasma is generated in the process chamber. The narrower this distance is, the more rapid the possible film formation is. Besides, if the frequency of the microwave supplied is within the range not less than 900 MHZ and not more than 10 GHz, the same result as that described below can be obtained. The distance between the shower plate 102 and the substrate 103 is set at 6 cm in this embodiment. Although an example wherein film formation was done using the plasma apparatus with the radial line slot antenna was shown in this embodiment, the microwave may be introduced into the

process chamber using another method.

[0016]

In the high density plasma of the mixture gas of Kr and O_2, Kr* in an intermediate excitation state collides with an O_2 molecule, and atomic oxygen O* is efficiently generated. With this atomic oxygen, the substrate surface is oxidized. Until now, for example, oxidation of silicon surfaces was made with H_2O molecules or O_2 molecules, and the process temperatures were very high as 800 to 1100°C. However, oxidation with atomic oxygen is possible at a sufficiently low temperature. To increase opportunities of collision between Kr* and O_2, the higher process chamber pressure is desirable. But, if the pressure is too high, generated O* radicals collide with each other and return to an O_2 molecule. Of course, there is the optimum gas pressure. Fig. 1 shows the oxide film thickness that grows through an oxidation process at a silicon substrate temperature of 400°C for ten minutes, when the gas pressure in the process chamber is changed while the pressure ratio in the process chamber is kept at 97% Kr/3% oxygen. When the gas pressure in the process chamber is 1 Torr, the oxide film becomes the thickest. This pressure or its vicinity is optimal.

[0017]

Fig. 3 shows the relation between the oxide film thickness and the oxidation time upon silicon substrate surface oxidation using Kr/O_2 high density

plasma. Fig. 3 also shows the dependence on the oxidation time in conventional dry oxidation, in relation to substrate temperatures 800°C, 900°C, and 1000°C. It is clear that the oxidation speed of the Kr/O_2 high density plasma oxidation when the substrate temperature is 400°C and the pressure in the process chamber is 1 Torr (133 Pa) is higher than that of the atmospheric pressure dry O_2 oxidation when the substrate temperature is 1000°C. Introduction of silicon substrate surface oxidation using Kr/O_2 high density plasma considerably improves productivity of the surface oxidation technique. Further, in a conventional high-temperature thermal oxidation technique, O_2 molecules or H_2O molecules pass through the oxide film formed on the surface, by diffusion. They reach the interface between silicon/silicon oxide film and contribute to oxidation. Thus it was common knowledge that the oxidation speed is greatly influenced by the diffusion speed of O_2 or H_2O molecules in the oxide film, and increases in proportion to $t^{1/2}$ with the oxidation time t. In this case of Kr/O_2 high density plasma, however, the oxidation speed is linear till 35 nm of the oxide film thickness. This shows that atomic oxygen can freely pass through the silicon oxide film. Namely, it is clear that the diffusion speed is very high.

[0018]

Fig. 4 shows a result of an examination in which the distribution along depth of the Kr density in a

silicon oxide film formed through the above-described process was examined with a full-reflection fluorescence X-ray spectrometer. The examination was done under the conditions that the partial pressure of oxygen in Kr was 3%, the pressure in the process chamber was 1 Torr (133 Pa), and the substrate temperature was 400°C. The thinner the oxide film thickness is, the more the Kr density decreases. At the silicon oxide film surface, Kr exists at a density of about 2×10^{11} cm^{-2}. That is, this silicon oxide film is a film in which the Kr concentration in the film of the thickness of 4 nm or more is constant and the Kr concentration decreases toward the interface between silicon/silicon oxide film.

[0019]

Fig. 5 shows kinds of rare gases (Kr, Ar, He) used in silicon oxide film growth, and a result of an examination in which the ratio in composition of oxygen to silicon in silicon oxide films obtained was examined with an X-ray photoelectron spectrometer. Formation of the silicon oxide films was done with the apparatus shown in Fig. 1 at a substrate temperature of 400°C. The partial pressure of oxygen in each rare gas and the pressure in the process chamber were fixed at 3% and 1 Torr (133 Pa), respectively. For comparison, the ratio in composition of oxygen to silicon in a thermal oxide film formed at a substrate temperature of 900°C in the atmosphere of 100% oxygen is also shown. In case of

using helium gas (He) or argon gas (Ar), the composition ratio of the silicon oxide film shows poorness of oxygen. Contrastingly, the silicon oxide film formed using Kr gas shows the ratio of oxygen to silicon equivalent to that of the thermal oxide film. We suspect this is because the excitation state of Kr very efficiently generates O* in comparison with He or Ar.

[0020]

Fig. 6 shows kinds of rare gases used in silicon oxide film growth, and a result of an examination in which the interface level density in silicon oxide films obtained was examined through low-frequency C-V measurement. Formation of the silicon oxide films was done with the apparatus shown in Fig. 1 at a substrate temperature of 400°C. The partial pressure of oxygen in each rare gas and the pressure in the process chamber were fixed at 3% and 1 Torr, respectively. For comparison, the interface level density in a thermal oxide film formed at a substrate temperature of 900°C in the atmosphere of 100% oxygen is also shown. The interface level density of the oxide film formed using Kr gas is the lowest and it is equivalent to the interface level density of the thermal oxide film formed in the dry oxidation atmosphere at 900°C.

[0021]

Fig. 7 shows the relation between kinds of rare gases and activating energy for silicon oxide film

growth calculated from silicon oxide film growing speed. Formation of silicon oxide films was done with the apparatus shown in Fig. 1 at substrate temperatures within the range of 200 to 400°C. The partial pressure of oxygen in each rare gas and the pressure in the process chamber were fixed at 3% and 1 Torr (133 Pa), respectively. In case of oxidation using helium gas (He) and argon gas (Ar), the activating energies are high as 0.5 eV and 0.8 eV, respectively. In case of using Kr gas, however, the activating energy can be held down to 0.13 eV. That is, if the dependence on temperature is very low and atomic oxygen is efficiently generated, even at a low temperature as 200°C, a sufficiently high oxidation speed is realized.

[0022]

Fig. 8 shows a result of examination of the relations between the oxygen partial pressure in Kr in a silicon oxide film formation atmosphere, the withstand voltage of a silicon oxide film, and the interface level density in a silicon oxide film formed. In this case, the pressure in the process chamber was fixed at 1 Torr (133 Pa). When the oxygen partial pressure in Kr is 3%, the interface level density becomes the minimum and its value equivalent to the interface level density in a thermal oxide film is obtained. Besides, the withstand voltage of the silicon oxide film becomes the maximum also in the vicinity of 3% of the oxygen

partial pressure. From the result of Fig. 8, the oxygen partial pressure upon oxidation using Kr/O_2 mixture gas is suitably 2 to 4%.

[0023]

Fig. 9 shows the relations between pressure upon silicon oxide film formation, and the withstand voltage and the interface level density of a silicon oxide film. In this case, the oxygen partial pressure was 3%. When the pressure upon film formation is near 1 Torr, the withstand voltage of the silicon oxide film becomes the maximum and the interface level density becomes the minimum. From this, when an oxide film is formed using Kr/O_2 mixture gas, the pressure upon film formation is optimally 800 to 1200 mTorr.

[0024]

Fig. 10 shows the current-voltage characteristics of 3.5 nm, 5.0 nm, 7.8 nm, and 10 nm-thick silicon oxide films obtained with microwave (2.45 GHz)-excited high density plasma of Kr/O_2 = 97%/3% at a substrate temperature of 400°C when a positive voltage is applied through electrodes to inject electrons into the silicon oxide films from the substrate side. For reference, the characteristics in case of the same thickness and 1000°C dry oxidation are also shown. In the lower electric field region, the electric currents of the silicon oxide films grown with Kr/O_2 are less than those of the thermal oxide films. In the higher electric field region, both films show

quite the same characteristics.

[0025]

Fig. 11 shows the J/E^2-I/E characteristic, i.e., the F-N characteristic when the current density flowing through a silicon oxide film formed with microwave (2.45 GHz)-excited high density plasma of Kr/O_2 = 97%/3% is J (A/cm^2), and the electric field intensity is E (MV/cm). Although three kinds in thickness of silicon oxide films were used, i.e., 5.0 nm, 7.8 nm, and 10 nm, the same characteristic was obtained almost irrespective of film thickness. It is found that F-N currents between 10^{-13} to 10^{-22}, i.e., over the range of nine figures, flow. The barrier height between silicon/silicon oxide films is 3.2 eV.

[0026]

Fig. 12 shows the breakdown fields of silicon oxide films formed with microwave (2.45 GHz)-excited high density plasma of Kr/O_2 = 97%/3%, and 1000°C dry-oxide films in relation to three kinds of films, i.e., 3.5 nm, 5.0 nm, and 7.8 nm as (a), (b), and (c), respectively. In any thickness obtained were quite the same breakdown field intensities as those of the corresponding thermal oxide film.

[0027]

Fig. 13 shows the amounts of charges QBD (Charge-to-Breakdown) till silicon oxide films are broken down when a stress current of 1 A/cm^2 is applied from the substrate side, in relation to Kr/O_2 high density plasma oxidation, 800°C wet oxidation, and 900°C dry

oxidation. The thickness is 5.0 nm. The silicon oxide film grown with Kr/O_2 high density plasma shows its QBD value higher than those of 800°C wet oxidation and 900°C dry oxidation.

[0028]

As for the above-described various characteristics, even though oxidation was done at a low temperature as 400°C, the oxide films grown with Kr/O_2 high density plasma show the characteristics superior to those of the conventional high-temperature thermal oxide films. We suspect this is because the stress in the oxide film or at the Si/SiO_2 interface is relaxed by Kr being contained in the film, the charges in the film and the interface level density are reduced, and thereby the electrical characteristics of the silicon oxide film are considerably improved. In particular, we suspect that containing Kr at a surface density of 5×10^{11} cm^{-2} or less contributes to the improvement of the electrical characteristics of the silicon oxide film.

[0029]

Fig. 14 shows the subthreshold characteristics of MOS transistors formed on monocrystalline silicon substrates, which figure shows the characteristics when a gate oxide film formed with the apparatus of Fig. 1 using Kr/O_2 high density plasma at a substrate temperature of 400°C and a conventional gate oxide film formed by about 900°C thermal oxidation are used as the gate insulating films. The subthreshold

characteristic (marks ○ in the figure) of the MOS transistor with its gate oxide film formed using the apparatus of Fig. 1 shows substantially the same characteristic as the subthreshold characteristic (marks ● in the figure) of the gate oxide film by thermal oxidation.

[0030]

Fig. 15 shows the relation between the drain current and the gate voltage of MOSFET. In the figure, marks ○ represent a case wherein a Kr/O_2 plasma oxide film is used as the gate insulating film, and, in the figure, marks ● represent a case wherein a thermal oxide film is used as the gate insulating film. The oxide film thickness is 10 nm. Both show quite the same characteristic.

[0031]

It was proved that sufficiently high quality semiconductor device formation is possible using low-temperature formed gate insulating films.

[0032]

To realize an oxide film of the present invention, another plasma process apparatus that enables low-temperature oxide film formation using plasma may be used. For example also possible is formation with a two-stage shower plate type plasma process apparatus having first gas discharging means for discharging Kr gas for exciting plasma by a microwave, and second gas discharging means for discharging oxygen gas different from the above first gas discharging means.

[0033]

[Embodiment 2]

Fig. 16 shows conceptional views of a shallow trench isolation. This shallow trench isolation is formed by the manner that a silicon substrate 1603 surface is etched with plasma, a silicon oxide film 1602 formed by a CVD method is formed on the silicon substrate surface after being etched, and further the silicon oxide film formed is polished using a CMP method. After polishing, sacrificial oxidation is done by exposing the silicon substrate to a 800 to 900°C oxidative atmosphere. A silicon oxide film formed by the sacrificial oxidation is etched off in a liquid chemical containing fluoric acid to obtain a highly pure silicon surface. After this, the substrate surface is cleaned using RCA cleaning, and a gate insulating film 1601 is formed. When a conventional thermal oxidation method was used for the gate insulating film formation process, irrespective of formation conditions (dry oxidation or wet oxidation, or formation temperature), as shown in Fig. 17, thinning of the silicon oxide film was confirmed at an edge portion of the shallow trench isolation. Contrastingly, when the silicon oxide film is formed by oxidation using Kr/O_2 high density plasma according to the present invention, thinning of t the silicon oxide film does not occur at the edge portion of the shallow trench isolation.

[0034]

Fig. 18 shows the QBD characteristics when the gate oxide film of a MOS capacitor having a shallow trench isolation structure is formed by 800°C wet oxidation, and when a silicon oxide film is formed by oxidation using Kr/O_2 high density plasma. As stress, electric charges were injected from the substrate side toward the silicon oxide film with a low electric current of 1 A/cm^2. It was confirmed that QBD of the silicon oxide film formed by 800°C wet oxidation had a wide distribution on the lower QBD side caused by thinning at an shallow trench isolation edge portion, and the reliability of the device was bad. However, the QBD characteristic of the silicon oxide film formed by oxidation using Kr/O_2 high density plasma is very uniform. This is because thinning of the silicon oxide film thickness does not occur at the shallow trench isolation edge portion. By using the silicon oxide film formation technique of the present invention, the reliability of the device was considerably improved.

[0035]

Fig. 19 shows the relation between the taper angle of the shallow trench isolation and the thinning rate of the silicon oxide film. In a silicon oxide film formed by a thermal oxidation method, as the taper angle increased, thinning at an shallow trench isolation edge portion went intensive, and it was hard to make the taper angle less than 75 degrees for ensuring the device reliability. When

the silicon oxide film is formed by oxidation using Kr/O_2 high density plasma according to the present invention, even if the taper angle increases to more than 75 degrees, the uniformity of the silicon oxide film can be held down to 30% or less even at the shallow trench isolation edge portion. Because it is possible to ensure the reliability even if the taper angle of the shallow trench isolation is increased, because the area of the element isolating region reduces, further improvement of integration of semiconductor elements becomes possible.

[0036]

[Embodiment 3]

Gate oxidation with Kr/O_2 microwave-excited high density plasma using the apparatus of Fig. 1 is optimal for integrated device fabrication on a metallic substrate SOI wafer in which a conventional high-temperature process can not be used.

Fig. 20 is a sectional view of MOS transistors made on a metallic substrate SOI. Reference numeral 2001 denotes n++, p++ low-resistance semiconductor, 2002 does a silicide layer such as NiSi, 2003 does a conductive nitride layer such as TaN or TiN, 2004 does a metal layer such as Cu, 2005 does a conductive nitride layer such as TaN or TiN, 2006 does n++, p++ low-resistance semiconductor layer, 2007 does a nitride insulating film such as AlN or Si_3N_4, 2008 does a SiO_2 film, 2009 does an insulating film of SiO_2, BPSG, or a combination of them, 2010 does an n++

drain region, 2011 does an N++ source region, 2012 does a p++ drain region, 2013 does a P++ source region, 2014 and 2015 do a high-resistance semiconductor layer, 2016 does a SiO_2 film formed with Kr/O_2 microwave-excited high density plasma according to the present invention, 2017 and 2018 do an nMOS gate electrode and a pMOS gate electrode made of, e.g., Ta, Ti, TaN/Ta, TiN/Ti, or the like, 2019 does a nMOS source electrode, and 2020 does nMOS and pMOS drain electrodes. Reference numeral 2021 denotes a pMOS source electrode. Reference numeral 2022 denotes a substrate surface electrode. For the substrate including a Cu layer protected by TaN or TiN, the thermal treatment temperature must be 700°C or less in order to suppress the diffusion of Cu. The n++, p++ source/drain regions are formed by a thermal treatment of 550°C after ion implantation of As+, AsF_2+, or BF_2+. Until now, there was no technique for forming a high-quality oxide film at 700°C or less. By Kr/O_2 microwave-excited high density plasma oxidation, fabrication of the metallic substrate SOIMOSLSI shown in Fig. 20 first became possible.

[0037]

Fig. 21 is a conceptional view of a SOI device. Using this device structure, in case that a thermal oxide film was used for the gate insulating film, and in case that the gate insulating film was formed by oxidation using Kr/O_2 high density plasma, the

subthreshold characteristics of transistors are shown in Figs. 22. When the gate insulating film was formed by thermal oxidation, in the subthreshold characteristic, a kink due to bad coverage of the silicon oxide film is observed. When the gate insulating film was formed by oxidation using Kr/O_2 high density plasma, any kink is not observed in the subthreshold characteristic. Even in case of using a mesa type isolation structure, by forming the gate insulating film by oxidation using Kr/O_2 high density plasma, considerable improvement of reliability is possible.

[0038]

[Embodiment 4]

Fig. 23 is a conceptional view showing an example of apparatus for oxidizing a rectangular substrate such as a glass substrate or a plastic substrate. A vacuum vessel (process chamber) 2307 is put in a depressurized state, Kr/O_2 mixture gas is introduced through a shower plate 2301, gas is discharged through a thread groove pump 2302, and, for example, the pressure in the process chamber is set at 1 Torr. A glass substrate 2303 is placed on a sample table 2304 with a heating system, and, for example, setting is made such that the temperature of the glass substrate becomes 300°C. A microwave is supplied from a slit of a rectangular waveguide tube 2305 through a dielectric plate 2306 into the process chamber to generate high density plasma in the process chamber.

The shower plate 2301 serves also as a waveguide where the microwave radiated from the waveguide tube is propagated to the right and left as a surface wave. [0039]

Fig. 24 shows a conventional TFT device structure of an inverse-stagger structure and an improved TFT device structure. On the back surface of the glass substrate of the improved TFT device structure, the ITO film 2413 is formed to improve the close contact between the substrate and the susceptor of the film formation apparatus by an electrostatic chuck, and prevent improvement of reliability/uniformity of process, in particular, device break and deterioration of device characteristics due to static electricity. Although a silicon nitride film is used for the gate insulating film 2403 like the prior art, since considerable improvement of its withstand voltage has succeeded, the thickness of the silicon nitride film can be decreased to the degree of 100 to 200 nm though it conventionally required about 400 nm. By thinning the silicon nitride film to a half, it becomes possible to improve the current drive performance of the TFT device substantially twice. [0040]

In the improved TFT device structure, since not the n+ amorphous silicon layer between the source 2405 and the drain 2407 is etched by RIE, but the n+ amorphous silicon layer is directly oxidized with the apparatus of Fig. 23 to insulate, the non-doped

amorphous silicon layer 2404 as the channel is never exposed to high-energy ion irradiation. Therefore, the non-doped amorphous silicon layer 2404 can be thinned from 150 nm to about 30 nm. When the thickness of the non-doped amorphous silicon layer 2404 as the channel becomes 1/5, since the resistance of the spatial charge layer becomes about 1/25, the current drive performance of the TFT device becomes 20 to 30 times. Because the thickness of the non-doped amorphous silicon layer 2404 could be decreased to about 1/5 or less, the amount of generated electron-hole pairs by a back light also could be decreased to about 1/5 or less, and the dynamic range of the luminance of the LCD display section can be improved by nearly one figure.

[0041]

Fig. 25 shows the relation between the gate voltage and the drain current of TFT devices. In comparison with the conventional TFT device, the drain current of the improved TFT device is considerably increased, and it shows that the characteristic is considerably improved. Simultaneously, the leakage current upon reverse biasing is also decreased. This is because the interface characteristic between the non-doped amorphous silicon and the SiO_2 layer is improved.

[0042]

[Embodiment 5]

Fig. 26 shows a sectional structure of

polysilicon TFTs made for a peripheral circuit of a display unit such as an LCD. Reference numeral 2601 denotes a glass substrate or a plastic substrate, 2602 does an Si_3N_4 film, 2603 does the channel layer of a polysilicon pMOS, 2605 and 2606 do the source region and the drain region of a polysilicon nMOS, respectively, and 2607 and 2608 do the source region and the drain region of the pMOS, respectively. Reference numeral 2609 denotes a SiO_2 layer according to the present invention, wherein a uniformly thick silicon oxide film at either of its flat portion and its edge portion is formed on polysilicon. Reference numeral 2610 denotes the gate electrode of the polysilicon nMOS, 2611 does the gate electrode of the polysilicon pMOS, 2612 does an insulating film such as SiO_2, BSG, or BPSG, 2613 and 2614 do a source electrode and a drain electrode (simultaneously a drain electrode of the polysilicon pMOS) of the polysilicon nMOS, 2615 does a source electrode of the polysilicon pMOS, and 2616 does a transparent electrode such as surface ITO.

[0043]

Besides, the present invention is applied also to polysilicon TFTs made for a peripheral circuit of a display unit such as an LCD, as shown in Fig. 27. Reference numeral 2701 denotes a glass substrate or a plastic substrate, 2702 does an Si_3N_4 film, 2703 does the channel layer of a polysilicon pMOS, 2705 and 2706 do the source region and the drain region of a

polysilicon nMOS, respectively, and 2707 and 2708 do the source region and the drain region of the pMOS, respectively. Reference numeral 2709 denotes a SiO_2 layer according to the present invention, wherein the oxide film is not thinned even at the corners of the element isolating region between the transistors, and a uniformly thick silicon oxide film at either of its flat portion and its edge portion is formed on polysilicon. Therefore, the electrical characteristics/reliability of the device were remarkably improved. Reference numeral 2710 denotes the gate electrode of the polysilicon nMOS, 2711 does the gate electrode of the polysilicon pMOS, 2712 does an insulating film such as SiO_2, BSG, or BPSG, 2713 and 2714 do a source electrode and a drain electrode (simultaneously a drain electrode of the polysilicon pMOS) of the polysilicon nMOS, 2715 does a source electrode of the polysilicon pMOS, and 2716 does a transparent electrode such as surface ITO. Fig. 28 is another sectional structure of a polysilicon TFT made for a peripheral circuit of a display unit such as an LCD. This structure was made by the manner that the polysilicon layers 2703 and 2704 were formed on the Si_3N_4 film 2702, and, after etching the polysilicon layers, a gate insulating film was formed by plasma oxidation using Kr, and further the polysilicon electrode was formed.

[0044]

In the apparatus shown in Fig. 23, using a two-

stage shower plate microwave-excited high density plasma apparatus in which a two-stage shower plate has been further introduced, when inert gas such as Ar, Kr, or Xe is supplied through the first stage shower plate and material gas such as SiH_4 is supplied through the second stage shower plate, the electron mobility in polysilicon formed is 200 to 400 $cm^2/Vsec$ at a substrate temperature of about 300°C. If the channel length is set at about 1.5 to 2.0 μm, sufficiently high-speed signal processing beyond 100 MHz becomes possible. Most peripheral circuits required for driving a display unit such as an LCD can be made.

[0045]

[EFFECT]

As has been described, according to the present invention, it becomes possible to realize a high-quality silicon oxide film superior to a conventional thermal oxide film formed at a high temperature of about 1000°C, at a low temperature of a substrate temperature of 200 to 500°C.

[0046]

Besides, since the thickness of the silicon oxide film at a portion near a corner of a silicon oxide film element isolation side wall portion becomes generally equal to the thickness of a flat silicon surface portion, the characteristics such as leakage current and withstand voltage of the oxide film become good, and an improvement of the reliability of

the element and an improvement of the drive performance of the MOS transistor can be realized.

[0047]

Besides, even if the angle of the side wall portion of the recess portion of the element isolating region formed on a silicon substrate, with the silicon surface is set at 70 degrees or more or 90 degrees, thinning of the silicon oxide film at a corner of the side wall portion does not occur, it becomes possible to form a narrow element isolating region, the ratio of an effective area for forming elements such as transistors is increased, and high density integration can be realized.

[0048]

Further, even in the element isolation structure for integrated elements of SOI (Silicon On Insulator) transistors and polysilicon transistors formed on an insulating film, a high-quality oxide film can be formed on the element isolation side wall portion, and, without any parasitic transistor existing, the electrical characteristics of the transistors can be good. By using the silicon oxide film formation method of the present invention, a very high-quality silicon oxide film can be formed even though it is formed at a low temperature as a substrate temperature of 200 to 500°C. By this, fabrication of high-performance amorphous silicon TFTs or polysilicon TFTs on a metallic substrate SOILSI, a glass substrate, or a plastic substrate which was

conventionally impossible becomes possible, so the effect is great.

[0049]

[BRIEF DESCRIPTION OF THE DRAWINGS]

[FIG. 1]

Fig. 1 is a conceptional view showing an example of apparatus using a radial line slot antenna for realizing a silicon oxide film formation method of the present invention.

[FIG. 2]

Fig. 2 is a graph showing the dependence of oxidation film thickness on process chamber gas pressure in a high density plasma oxidation process at a substrate temperature of 400°C, Kr/O_2 = 97/3, and 2.45 GHz for ten minutes.

[FIG. 3]

Fig. 3 is a graph showing the dependence of oxidation film thickness on oxidation time in a high density plasma oxidation process at a substrate temperature of 400°C, Kr/O_2 = 97/3, and 2.45 GHz, as well as dependence on oxidation time in conventional dry oxidation (at substrate temperatures of 800°C, 900°C, and 1000°C).

[FIG. 4]

Fig. 4 is a graph showing the distribution along depth of Kr density in a silicon oxide film.

[FIG. 5]

Fig. 5 is a graph showing kinds of rare gases used in silicon oxidation, and ratios in composition

of oxygen to silicon in silicon oxide films obtained.

[FIG. 6]

Fig. 6 is a graph showing kinds of rare gases used in growths of silicon oxide films, and a result of measurement of interface level densities of the silicon oxide films obtained.

[FIG. 7]

Fig. 7 is a graph showing a result of examination of the relation between kinds of rare gases and activating energy for silicon oxide film growth calculated from silicon oxide film growing speed.

[FIG. 8]

Fig. 8 is a graph showing a result of examination of the relations between oxygen partial pressure in Kr in a silicon oxide film formation atmosphere and interface level density in a silicon oxide film formed and its withstand voltage.

[FIG. 9]

Fig. 9 is a graph showing a result of examination of the relations between the whole pressure in a process chamber in a silicon oxide film formation atmosphere and interface level density in a silicon oxide film formed and its withstand voltage.

[FIG. 10]

Fig. 10 is a graph showing the current-voltage characteristics of 3.5 nm, 5.0 nm, 7.8 nm, and 10 nm-thick silicon oxide films obtained with microwave (2.45 GHz)-excited high density plasma of Kr/O_2 = 97%/3% at a substrate temperature of 400°C when

electrons have been injected from the substrate side and a positive voltage is applied through electrodes (for reference, the characteristics in case of the same thickness, 1000°C, and dry oxidation are also shown).

[FIG. 11]

Fig. 11 is a graph showing the J^2/E-I/E characteristic, i.e., the F-N characteristic when the current density flowing through a silicon oxide film formed with microwave (2.45 GHz)-excited high density plasma of Kr/O_2 = 97%/3% is J (A/cm^2), and the electric field intensity is E (MV/cm) (three kinds in thickness of silicon oxide films are used, i.e., 5.0 nm, 7.8 nm, and 10 nm).

[FIG. 12]

In Fig. 12, (a),(b) and (c) are graphs showing the breakdown fields of silicon oxide films formed with microwave (2.45 GHz)-excited high density plasma of Kr/O_2 = 97%/3%, and 1000°C dry-oxide films in relation to three kinds of films, i.e., 3.5 nm, 5.0 nm, and 7.8 nm, respectively.

[FIG. 13]

Fig. 13 is a graph showing the amounts of charges QBD (Charge-to-Breakdown) till silicon oxide films are broken down when a stress current of 1 A/cm^2 is applied from the substrate side, in relation to Kr/O_2 high density plasma oxidation, 800°C wet oxidation, and 900°C dry oxidation.

[FIG. 14]

Fig. 14 is a graph showing the subthreshold characteristics of MOS transistors formed on monocrystalline silicon substrates, which graph shows the characteristics when a gate oxide film formed with Kr/O_2 high density plasma at a substrate temperature of 400°C and a conventional gate oxide film formed by about 900°C thermal oxidation are used as the gate insulating films.

[FIG. 15]

Fig. 15 is a graph showing the relation between the drain current and the gate voltage of MOSFET (in the figure, marks ○ represent a case wherein a Kr/O2 plasma oxide film is used as the gate insulating film, and, in the figure, marks ● represent a case wherein a thermal oxide film is used as the gate insulating film).

[FIG. 16]

Fig. 16 shows conceptional views showing a shallow trench isolation structure.

[FIG. 17]

Fig. 17 shows conceptional views showing a difference in coverage between gate insulating films when the shallow trench isolation structure is applied to a prior art (a case of thermal oxidation) and the present invention (oxidation with Kr/O2 high density plasma).

[FIG. 18]

Fig. 18 is a graph showing a difference between the QBD characteristics of MOS capacitors when the

shallow trench isolation structure is applied to a prior art (a case of thermal oxidation) and the present invention (oxidation with Kr/O_2 high density plasma).

[FIG. 19]

Fig. 19 is a graph showing the relation between the shallow trench isolation taper angle and the edge portion film thinning rate when the shallow trench isolation structure is applied to a prior art (a case of thermal oxidation) and the present invention (oxidation with Kr/O_2 high density plasma).

[FIG. 20]

Fig. 20 is a sectional view of MOS transistors made on a metallic substrate SOI.

[FIG. 21]

Fig. 21 is a sectional view of MOS transistors made on a SOI substrate.

[FIG. 22]

Fig. 22 shows graphs showing subthreshold characteristics when a gate insulating film of a device is applied to a prior art (a case of thermal oxidation) and the present invention (oxidation with Kr/O_2 high density plasma).

[FIG. 23]

Fig. 23 is a conceptional view of a microwave-excited high density plasma apparatus for glass substrates and plastic substrates.

[FIG. 24]

Figs. 24 are sectional views showing a

conventional TFT device structure and an improved TFT device structure.

[FIG. 25]

Fig. 25 is a graph showing a result of measurement of the relation between the gate voltage and the drain current of TFT devices.

[FIG. 26]

Fig. 26 is a sectional view of polysilicon TFTs for driving a display section such as an LCD.

[FIG. 27]

Fig. 27 is a sectional view of polysilicon TFTs for driving a display section such as an LCD.

[FIG. 28]

Fig. 28 is another sectional view of a polysilicon TFT for driving a display section such as an LCD.

[EXPLANETION OF CODES]

101 process chamber

102 shower plate

103 silicon wafer

104 sample table with a heating system

105 coaxial waveguide tube

106 radial line slot antenna

107 dielectric plate

1601 gate insulating film

1602 CVD oxide film

1603 silicon substrate

1701 gate insulating film

1702 CVD oxide film

1703 silicon substrate

2001 n++, p++ low-resistance semiconductor

2002 silicide layer such as NiSi

2003 conductive nitride layer such as TaN or TiN

2004 metal layer such as Cu

2005 conductive nitride layer such as TaN or TiN

2006 n++, p++ low-resistance semiconductor layer

2007 nitride insulating film such as AlN or Si_3N_4

2008 SiO_2 film

2009 insulating film of SiO_2, BPSG, or a combination of them

2010 n++ drain region

2011 n++ source region

2012 p++ drain region

2013 P++ source region

2014 high-resistance semiconductor layer

2015 high-resistance semiconductor layer

2016 SiO_2 film formed with Kr/O_2 microwave-excited high density plasma according to the present invention

2017 nMOS gate electrode and a pMOS gate electrode made of, e.g., Ta, Ti, TaN/Ta, TiN/Ti, or the like

2018 nMOS gate electrode and a pMOS gate electrode made of, e.g., Ta, Ti, TaN/Ta, TiN/Ti, or the like

2019 nMOS source electrode

2020 nMOS and pMOS drain electrodes

2021 pMOS source electrode

2022 substrate surface electrode

2101 silicon substrate

2102 SiO_2 film

2103 silicon oxide film formed by Kr/O_2 high density plasma

2104 insulating film of SiO_2, BPSG, or a combination of them

2105 n++ source region

2106 nMOS source electrode

2107 SiO_2 film

2108 nMOS gate electrode

2109 drain electrode

2110 n++ drain region

2111 p++ drain region

2112 nMOS and pMOS drain electrodes

2113 pMOS gate electrode

2114 pMOS gate electrode

2115 p++ source region

2116 n type silicon layer

2117 p type silicon layer

2301 shower plate

2302 thread groove pump

2303 glass substrate

2304 sample table with a heating system

2305 rectangular waveguide tube

2306 dielectric plate

2401 glass substrate or plastic substrate
2402 gate electrode (Ti/Al/Ti)
2403 gate insulating film (Si_3N_4)
2404 channel (non-doped amorphous silicon)
2405 source (n+ amorphous silicon)
2406 source electrode (Ti/Al/Ti)
2407 drain (n+ amorphous silicon)
2408 drain electrode (Ti/Al/Ti)
2409 interlayer dielectric film (Si_3N_4)
2410 pixel electrode
2411 silicon oxide film for insulating source/drain
2412 gate electrode (TaN/Cu)
2413 transparent electrode on back surface (ITO)

2601 glass substrate or plastic substrate
2602 Si_3N_4 film
2603 channel layer of a polysilicon nMOS
2604 channel layer of a polysilicon pMOS
2605 source region of a polysilicon nMOS
2606 drain region of a polysilicon nMOS
2607 drain region of a polysilicon pMOS
2608 source region of a polysilicon pMOS
2609 SiO_2 film
2610 gate electrode of a polysilicon nMOS
2611 gate electrode of a polysilicon pMOS
2612 insulating film such as SiO_2, BSG, or BPSG
2613 source electrode of a polysilicon nMOS

2614 drain electrode

2615 source electrode of a polysilicon pMOS

2616 transparent electrode such as surface ITO

2701 glass substrate or plastic substrate

2702 Si_3N_4 film

2703 channel layer of a polysilicon nMOS

2704 channel layer of a polysilicon pMOS

2705 source region of a polysilicon nMOS

2706 drain region of a polysilicon nMOS

2707 drain region of a polysilicon pMOS

2708 source region of a polysilicon pMOS

2709 SiO_2 film

2710 gate electrode of a polysilicon nMOS

2711 gate electrode of a polysilicon pMOS

2712 insulating film such as SiO_2, BSG, or BPSG

2713 source electrode of a polysilicon nMOS

2714 drain electrode

2715 source electrode of a polysilicon pMOS

2716 transparent electrode such as surface ITO

2801 polysilicon electrode

2802 SiO_2 film

2803 polysilicon layer

2804 insulating film such as SiO_2, BSG, or BPSG

2805 Si_3N_4 film

2806 glass substrate, plastic substrate

2807 transparent electrode such as surface ITO